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SELECTION OF A SCHEME FOR CERAMIC PRECURSOR SYNTHESIS

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Three schemes of synthesis of precursors for barium-titanate ceramics are considered. Water-hydrochloric acid media with application of isopropyl and butyl alcohols and water-hydrochloric acid media with introduction of hydrogen peroxide and subsequent ammonia hydrolysis are investigated. Methods of synthesis are discussed. The processes are monitored with the pH-meter method. The experimental results are processed according to probability theory and the random processes method. Predictions of the interdependence of the ingredients and their effect on the course of synthesis are made. Consumption of chemical reagents is optimized.

Processes involving liquids have received wide acceptance in the technology of synthesis of fine (ultradisperse) precursors for engineering ceramics. The literature data indicate that on one hand, the ample studies performed in this field intensely supplement the empirical database, and on the other hand, a universal theory of liquid-phase processes has apparently not yet been developed. In this context, it is advisable to develop specific criteria for each particular case of synthesis.

The purpose of the present paper was to substantiate the choice of a scheme for liquid-phase synthesis of precursors for barium-titanate ceramic production, provide predictions of the behavior of the reagents in the various stages of synthesis, and optimize consumption of materials.

The reaction of liquid reagents with titanium- and barium-containing ingredients was investigated with their simultaneous presence in the reaction system (basic synthesis), with their presence separate from each other (supplementary synthesis), and with hydrochloric acid, which in all cases was the initial reaction medium. The process was monitored by the pH-meter method. The protocols of the experiments reflected the data on the weight of the solid substances and the volume of liquids used, records of the measuring instrument (pH values), and differential values dpH/dV calculated on their basis (dV is the volume of a single aliquot, ml) [1].

The reagents used were barium oxide BaO; metallic titanium Ti VT 1-0; 35% hydrochloric acid HCl; 92.5% sulfuric acid H_2SO_4 ; 25% ammonia water NH_4OH ; 30% hydrogen peroxide H_2O_2 ; isopropyl alcohol C_3H_8O ; butyl alcohol $C_4H_{10}O$; twice-distilled water. A diagram of the synthesis set up is shown in Fig. 1.

Synthesis of the batch containing titanium and barium in water-acid medium using isopropyl alcohol (WAIPA) and butyl alcohol (WABA) was performed in the following order.

Metallic titanium chips were placed in the glass cell, HCl was added, and the cooler was connected. Dissolution proceeded with moderate heating for 3–4 h. Intense emission of gas was observed, and a dark-purple solution resulted. The solution was evaporated to the minimum permissible volume. Powdered barium oxide was introduced in the vessel with the cooled titanium-containing solution. In the beginning, intense emission of gas took place and soon stopped; nevertheless, the greater part of the compound remained undissolved.

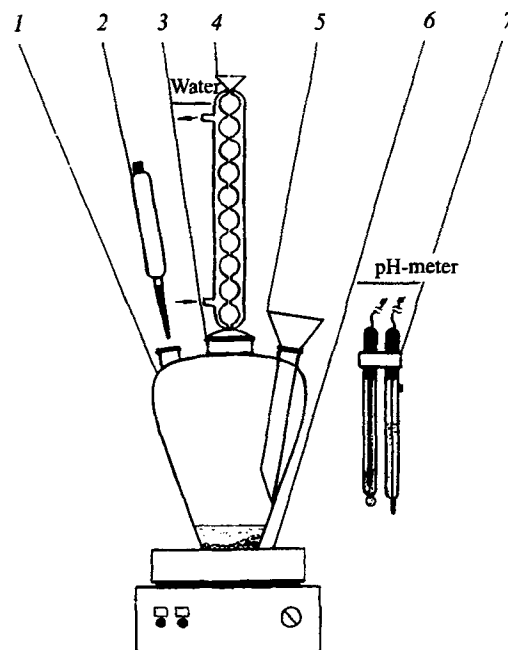


Fig. 1. Synthesis set: 1) three-neck glass cell; 2) pipette dosing apparatus; 3) cooler input and electrode unit; 4) cooler; 5) glass funnel; 6) electric heater (replaceable with magnetic stirrer); 7) electrode unit for pH-meter.

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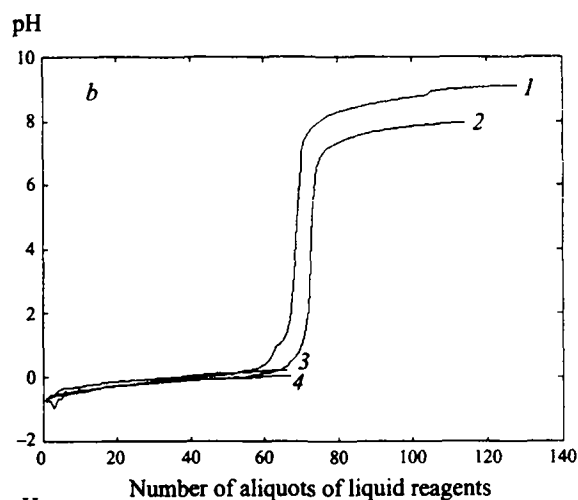
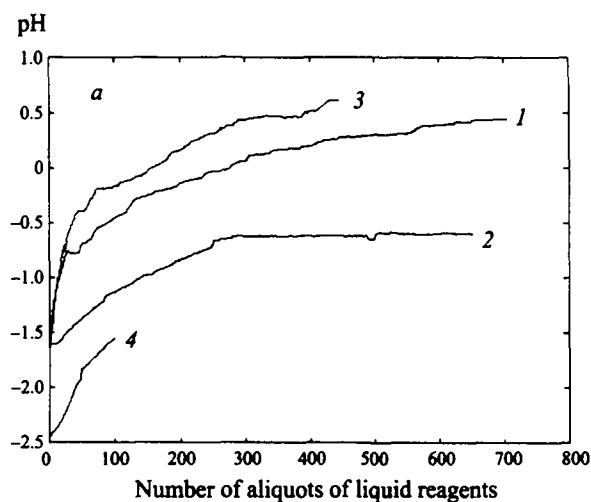
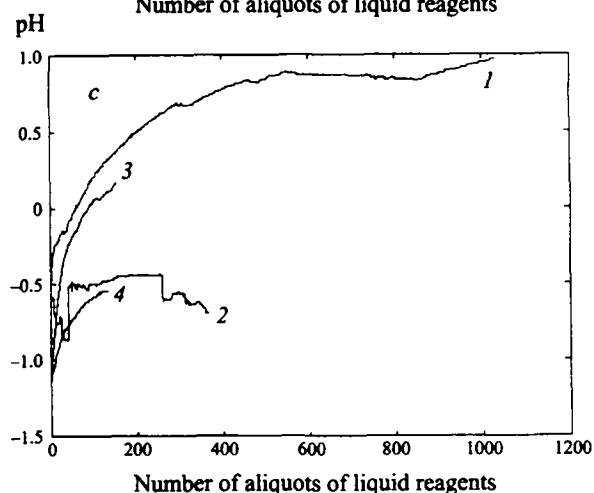


Fig. 2. pH Curves of synthesis in WAIPA (a), WABA (b), and WAPA (c) and treatment of HCl: 1) synthesis of titanium- and barium-containing batch; 2) synthesis of titanium-containing batch; 3) synthesis of barium-containing batch; 4) HCl treatment.



In the following stage, water (aliquots) was added to the reaction system through a dosing apparatus up to complete dissolution of the precipitate. After that alcohol was added by aliquots as well. In the course of this process, precipitation occurred several times. Water had to be added in order to dissolve the precipitate, and then alcohol was added again.

In the final stage of synthesis, no precipitation took place on introduction of alcohol, which pointed to completion of the process. As a result, a water-acid solution containing titanium and barium was formed whose color differed from the original color. Drying proceeded naturally, and with this a crystalline precipitate originated.

Synthesis of a titanium-containing batch in alcohol medium was carried out in the following way. In the beginning metallic titanium was dissolved, and then alcohol was added until the color of the solution changed.

For synthesis of a barium-containing batch in alcohol medium, barium oxide was introduced in HCl, upon which intense gas emission that soon stopped was observed. Part of the compound remained undissolved. Water was added, and then alcohol was added again. At the final stage, no precipitation occurred on introduction of alcohol, the color of the solution changed, and synthesis was terminated (as the medium was acid). Drying proceeded naturally.

Treatment of HCl with alcohol was monitored by the pH-meter method.

Synthesis of the batch containing titanium and barium in water-acid medium with addition of hydrogen peroxide and subsequent hydrolysis with ammonia (WAPA) proceeded in the following way.

The hydrochloric acid solution containing titanium was prepared according to the procedure described above.

In the first stage, H_2O_2 was added, and the color of the solution changed to an intense orange-red color. Next, BaO was introduced, intense gas emission took place, but the greater part of the compound remained undissolved.

In the second stage, water was added, and the precipitate dissolved.

In the third stage, NH_4OH was added to the reaction system. The first two or three aliquots caused opalescence, then a precipitate originated, and the color of the reaction system changed in the following order: intense red-orange, bright orange, bright yellow (on appearance of the bright yellow color, the contents of the glass cell represented a dense gel that was hard to stir), yellow, lemon-yellow, pale lemon color.

After the end of hydrolysis, the precipitate was left to settle and filtered, then washed with 0.5% aqueous solution of NH_4OH . The absence of barium and titanium ions in the

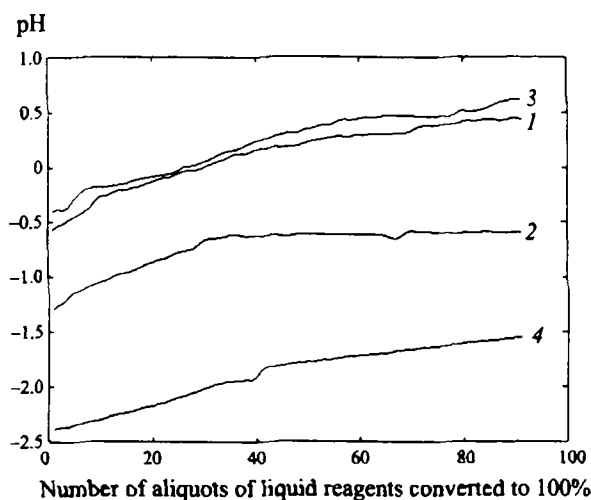


Fig. 3. Normalized pH-curves of synthesis in WAIPA and HCl treatment. Same designations as in Fig. 2.

filtrate and washing solution was monitored by performing qualitative reactions with H_2SO_4 and H_2O_2 , according to A. P. Kreshkov [2].

Synthesis of the titanium-containing batch in WAPA was carried out in the same way.

For synthesis of a barium-containing batch in WAPA, BaO was introduced in HCl. After the end of gas emission, H_2O_2 , H_2O , and NH_4OH were added to the reaction system (solid compound + solution). As a result, a colorless solution was obtained.

Experimental pH-curves are shown in Fig. 2.

Mathematical processing of the experimental results was carried out using probability theory and the random processes method [3, 4]. The terminology and symbols used in that theory were applied. Data on the dpH/dV differential values were used in the calculations. The first derivative of the pH had the meaning of a change in the rate of the acidity-basicity of the medium in each particular moment after addition of a fixed number of liquid reagents. For convenience, dpH/dV was designated as X . The data on X related to specific measurement conditions represented the spectra of discrete random values $\{X\}$.

For identification of X by synthesis stages, the following indexes are used: *aq* — the stage of introduction of water in the reaction system; *am* — the stage of adding ammonia; *sc* — synthesis of the batch containing titanium and barium from the solution (total batch); *tc* — synthesis of titanium-containing compound; *bc* — synthesis of barium-containing compound; *ac* — treatment of hydrochloric acid with the liquid reagents. The mutual correlation coefficients ρ of the solution components and linear regression coefficients (A and B) were calculated, and regression equations of the form [3, 4]

$$G(X) = AX + B,$$

were set up.

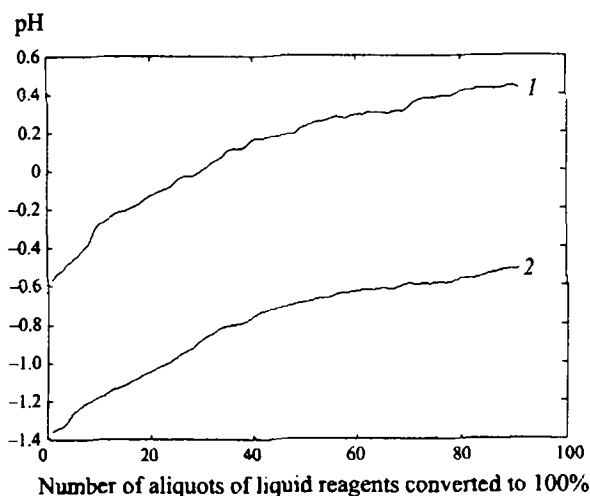
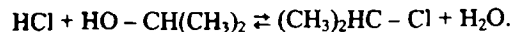
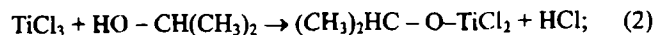
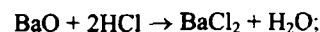


Fig. 4. Normalized pH-curves of synthesis of the batch containing barium and titanium in WAIPA: 1) actual; 2) mean arithmetic. Number of aliquots of liquid reagents converted to 100%.

By way of illustration, let us consider some results of the correlation regression analysis with respect to basic and supplementary batch synthesis according to the water-acid scheme with addition of isopropyl alcohol.

In synthesis involving isopropyl alcohol, a great effect was exhibited by HCl: $\rho_{ac-ac} = \rho_{ac-sc} = 29\%$ (the maximum value). The metallic ingredients had a similar effect on the process: $\rho_{sc-tc} = \rho_{tc-ac} \approx \rho_{sc-ac} = \rho_{ac-sc} = 18 - 19\%$.

The effect of HCl, as well as the effect of the total solution on HCl, depends upon the fact that in the beginning, the acid not bound with the metals and determining the medium participated in the synthesis. However, when the Cl-containing barium and titanium compounds reacted with the alcohol, HCl was generated as an intermediate reaction product and reacted again with the isopropyl alcohol. The simplified scheme of the process can be represented in the following way [5, 6].



Moreover, it was noted in [6] that titanium trichloride solution in isopropanol forms complexes of $\text{Ti}(\text{i-C}_3\text{H}_7\text{OH})_6\text{Cl}_3$ (purple color) or $\text{TiCl}_2 \cdot (\text{i-CH}(\text{CH}_3)\text{OH})_2 \cdot \text{CH}(\text{CH}_3)\text{OH}$ composition. Titanium in acid medium is capable of forming a whole series of complexes whose structure depends largely on the pH of the medium [2, 7]: $[\text{TiO}(\text{HO}_2)]$, $[\text{Ti}(\text{H}_2\text{O}_2)]^{4+}$, $[\text{TiO}(\text{O}_2)_2]^{2-}$, $[\text{Ti}(\text{OH})_2(\text{H}_2\text{O})(\text{H}_2\text{O}_2)]^{2+}$ (orange), $[\text{Ti}(\text{OH}_3)(\text{H}_2\text{O}_2)]^+$ (yellow) decomposing to $\text{Ti}(\text{OH})(\text{OOH})$. In addition to that, titanium oxychlorides can be formed (the fact of their existence is established, but the compounds have been little investigated, and the literature contains no reliable data on the oxychloride structure).

In the course of synthesis in water-hydrochloric acid medium with isopropyl alcohol, the overall solution had a significant effect on the terms of existence of the individual components in the system: titanium was affected to a lesser extent (titanium in chloride form is resistant to acid medium [8]), and barium and HCl experience this effect to a greater extent (for barium chloride dilute acid solutions are preferable [8]). This could happen because, taking into account the properties of titanium and barium and the conditions of the medium, a complex was probably formed which had titanium in its inner sphere, and barium and HCl molecules in the outer sphere. At certain moments, the coordination capacity of the outer sphere could decrease owing to Ba^{2+} and acid molecules splitting off. Besides, HCl was generated according to Eqs. (1) and (2).

Figures 3 and 4 illustrate the results of computer modeling of the experimental data. The abscissa represents the number of aliquots of liquid reagents converted to 100%. This made it possible to obtain the normalized pH-curves of different types of synthesis.

After summation of the pH curve ordinates (response functions or corresponding normalized values of the pH, assuming that no new compound was formed in the system), an arithmetic mean model curve was obtained.

It can be seen from Fig. 4 that the model and the actual pH curves do not coincide and differ in shape, i.e., the overall solution was not the mechanical sum of the solutions which

did not react with each other (independent from each other). In the course of introduction of isopropyl alcohol in the water-acid medium containing barium and titanium during the experiment, a new individual compound was formed. It is impossible to predict the quantitative output of the synthesis product relying only on computations.

The conclusions for synthesis in WABA and WAPA are similar.

A comparative analysis of the synthesis schemes was carried out in order to select the optimum scheme.

Synthesis following the first two schemes started and ended in acid medium.

The third scheme of synthesis started in acid medium as well, but its termination took place in basic medium. It can be arbitrarily divided into two parts: water-acid-peroxide part (WAP) (acid) and ammonium part (WAPa) (alkali).

Table 1 shows the results of the computation of the weight fractions of the probability of appearance of spectral values X belonging simultaneously to the mass data $\{X\}$ of all three patterns: 0, 0.02 (0.0176, 0.0206, 0.0235), and 0.04 (0.035).

It can be seen that in the case of alcohol synthesis (WAIPA and WABA), the time lag factor is quite significant (81.7 – 83.3%) when a reaction system does not react at all to an external effect (i.e. addition of liquid reagents). In this regard synthesis in WAP was more efficient: the time lag was only 2.3%. The absence of response ($X = 0$) signified that the reagents were not consumed and no reaction occurred.

In sum, the share of $X \neq 0$ amounted to 16.1, 16.5, and 29.6%, i.e., the reaction system in the case of WAP responded to an external effect twice as actively as in the cases of WAIPA and WABA. The alcohol systems responded in a similar way, and WAP had significant distinctions. The share of spectral values for which mass data $\{X\}$ did not overlap amounted to 2.1, 0.2, and 68.1, respectively. It may be inferred that in the case of the WAP stage, about 68% of the reagents were consumed for synthesis of a new compound.

The correlation of the total sums of the weight fractions revealed that WAIPA was 1.5 times shorter and WAP was 23 times shorter than the WABA scheme, that is, the process proceeded fastest in the case of the WAP scheme, therefore the WABA scheme is the least preferable.

Table 2 presents the coefficients of regression. The value of coefficient A standing before variable X in the regression equation allows a conclusion on whether the liquid reagent acts as medium or is a direct participant in the chemical reaction.

The isopropyl alcohol probably reacted with the acid titanium- and barium-containing solutions comprising the overall solution and with HCl ($A = 0.1263$, 0.1384 , and 0.1288 , respectively). At the same time the color transitions observed pointed to a chemical reaction. Butyl alcohol reacted more actively with HCl ($A = 0.1022$), more weakly with the barium-containing solution ($A = 0.0838$), and weakest of all with the titanium-containing component ($A = 0.0130$), where the alcohol fulfilled both the function of chemical reagent and medium (together with water and free HCl).

TABLE 1

| Spectral value | Weight fraction of probability of appearance (%) in synthesis in | | | |
|----------------|------------------------------------------------------------------|------|------|---------|
| | WAIPA | WABA | WAP | WAPa |
| 0 | 81.7 | 83.3 | 2.3 | 0.3 |
| 0.02 | 15.5 | 16.0 | 27.3 | 15.0 |
| 0.04 | 0.6 | 0.5 | 2.3 | No data |
| Total | 97.9 | 99.8 | 31.9 | 15.3 |

TABLE 2

| Type of synthesis | Type of dependence | Regression coefficient | |
|-------------------|--------------------|------------------------|--------|
| | | A | B |
| WAIPA | $sc - tc$ | 0.1263 | 0.0033 |
| | $sc - bc$ | 0.1384 | 0.0029 |
| | $sc - ac$ | 0.1288 | 0.0017 |
| WABA | $sc - tc$ | 0.0130 | 0.0034 |
| | $sc - bc$ | 0.0838 | 0.0021 |
| | $sc - ac$ | 0.1022 | 0.0033 |
| WAP | $sc - tc$ | 0.0168 | 0.0149 |
| | $sc - bc$ | 0.0508 | 0.0169 |
| | $sc - ac$ | 0.0327 | 0.0171 |
| WAPa | $sc - tc$ | 0.0013 | 0.1934 |
| | $sc - bc$ | 0.5180 | 0.1987 |
| | $sc - ac$ | 0.0542 | 0.1942 |

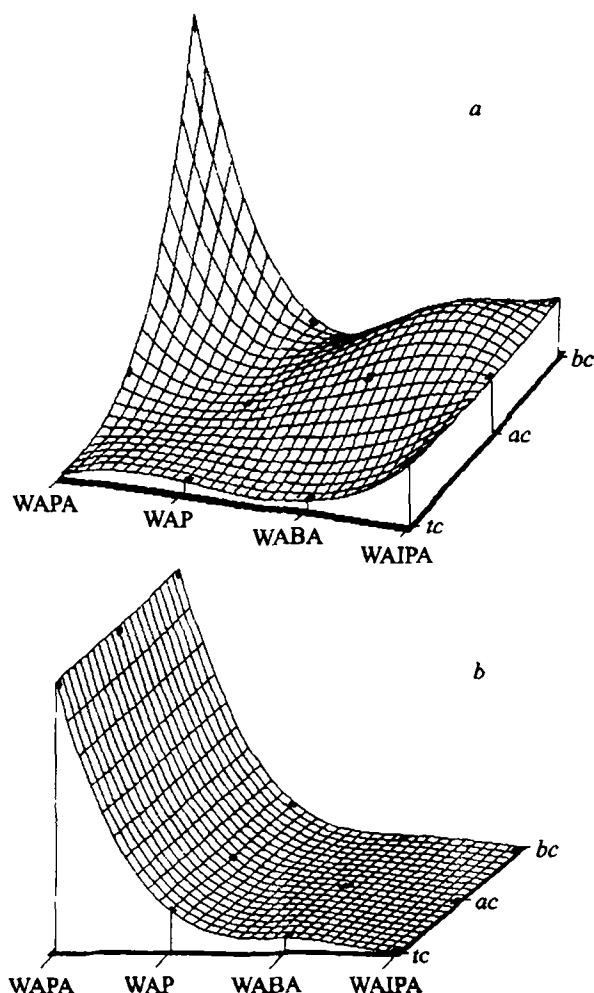


Fig. 5. Field of regression coefficients A (a) and B (b) depending on the synthesis pattern.

With synthesis in WAP, water acted mostly as a diluting agent for the HCl ($A = 0.0327$) and titanium-containing component ($A = 0.0168$). The barium-containing ingredient partly reacted chemically with the water and formed $\text{Ba}(\text{OH})_2$; however, hydroxide in HCl medium was instantly converted to the BaCl_2 form ($A = 0.0508$). Gradual dissolution of the precipitate was visually observed as water was gradually added.

It is possible to draw a conclusion on the sensitivity of the system to the reagents from the value of coefficient B in the regression equations.

The reaction systems exhibited low sensitivity to the effect of alcohols in synthesis (atmospheric pressure, ambient temperature, and catalysts were not used). However, with respect to water, the sensitivity in the WAP scheme increased by an order of magnitude and on average amounted to $B \approx 0.016$. This conclusion was supported by the different duration of different types of synthesis determined by the sum of aliquots of liquid reagents consumed. Of the acid schemes, synthesis without alcohol had obvious advantages.

Fig. 5 exhibits the A and B regression coefficient fields (Table 2) for the synthesis schemes considered. The graphic

TABLE 3

| Process | Consumption of reagents, ml* | | |
|---------------------------------|------------------------------|-------------------------------|--------------------|
| | H ₂ O | H ₂ O ₂ | NH ₄ OH |
| Synthesis of batch: | | | |
| titanium- and barium-containing | 29.92 | 2.04 | 52.36 |
| titanium-containing | 32.64 | 2.72 | 41.48 |
| barium-containing | 29.92 | 3.40 | 10.20 |
| HCl treatment | 34.00 | 2.72 | 8.20 |

* Initial amount of reacting ingredients: 1 g Ti; 22 ml HCl; 3.2 g BaO. TiO_2 : BaO ratio converted to oxides is 1 : 1.

form illustrates the effect of the overall solution containing a new synthetic compound on the components that have not reacted.

The results of mathematical processing of the experimental data proved that water-acid synthesis with addition of hydrogen peroxide and alkali ending with ammonia hydrolysis (WAPA) in the given conditions is the most promising method for production of precursors for barium-titanate ceramics.

The pH-meter control and calculation of the dpH/dV differential values made it possible to optimize consumption of the liquid reagents. The appearance of zero differential values (increase in system inertia) after a jump on the pH-curves was an indication for ceasing introduction of the reagents. It is easy to determine the total consumption of the liquid reagents from the number of aliquots introduced (Table 3).

Thus, the suggested approach using fairly simple pH-meter monitoring of batch synthesis, subsequent calculation of the dpH/dV differential values and their mathematical processing makes it possible to predict the behavior of each reagent in different stages of precursor synthesis for barium-titanate ceramics, to select the most promising scheme of synthesis, and to optimize consumption of the reagents.

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